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ORIGINS OF CALCITE IN A BOILING GEOTHERMAL SYSTEM

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ABSTRACT. The formation of hydrothermal calcite relates to the movement of carbon dioxide in a geothermal system as governed by boiling, dilution, and condensation. In this paper we show how these processes control the occurrence, distribution, and stable isotope composition of calcite based on a study at Broadlands-Ohaaki.

The two principal calcite occurrences in the Broadlands-Ohaaki geothermal system are: (1) as replacement of rock forming minerals and volcanic glass; and (2) as platy crystals infilling voids. Both are stable over a broad temperature range from <160° to >300°C. Replacement calcite is widespread and forms through hydrolysis reactions involving calcium alumino-silicates and sub-boiling liquids that contain 0.3 to 0.75 m CO_2. Platy calcite, in contrast, forms over a restricted vertical interval of a few hundred meters within the upflow zone. It precipitates from boiling fluids through exsolution of carbon dioxide as indicated by coeval liquid-rich and vapor-rich fluid inclusions and its formation in the two-phase zone.

Fluid inclusion data help to define the boiling paths of fluids from which platy calcite formed. Homogenization temperatures range from 160° to 310°C and are consistent within the present geothermal regime. Ice melting temperatures range from 0.0° to −1.0°C and indicate the presence of up to 0.5 m dissolved carbon dioxide. Model boiling curves calculated to match these data show how the concentration of dissolved carbon dioxide in the preboiled fluid dictates the depth of first boiling. Most fluid inclusion data lie along a model boiling path characteristic of the center of the upflow zone, in which the rising fluid (initially containing 0.75 m CO_2) begins to boil at ~320°C and ~2000 m depth; data from well Br-18 instead matches a curve in which the rising fluid (initially containing 0.53 m CO_2) begins boiling at ~245°C and ~900 m depth. The shallowing of the depth of first boiling likely results from dilution of dissolved carbon dioxide in the parent chloride water, as it rises and mixes with marginal waters.

Calcite precipitates from both shallow formed steam-heated groundwater and deeply derived chloride water, and these waters are isotopically distinct. At Broadlands-Ohaaki, the $\delta^{18}O$ values of calcite at >200°C range from 0.5 to 7.5 permil, whereas $\delta^{18}O$ values of calcite at <200°C range from 4 to 10 permil. Taking appropriate temperature dependent fractionation factors into account, these data indicate equilibration with chloride water ($\delta^{18}O_{H_2O} = -4.5$ permil) and steam-heated ground water ($\delta^{18}O_{H_2O} = -7.0$ permil), respectively. Oxygen isotopes of hydrothermal calcites in the nearby Wairakei and Waiotapu geothermal systems show similar patterns, consistent with the occurrence of both chloride and steam-heated waters there.

Calcite formation is explained by a model that describes the distribution of two-phase conditions and aqueous carbon dioxide concentra-

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tions in a column of hydrothermal fluid rising through a rock matrix of isotropic permeability. In this ideal situation, platy calcite forms along the inner margin of the two-phase zone, having the shape of an inverted cone, whereas replacement calcite mostly forms in the surrounding one-phase liquid-only zone. The sparse occurrence of calcite at ≤800 m depth in the central upflow of the Ohaaki sector at Broadlands-Ohaaki is compatible with this model and appears related to the exsolution of dissolved carbon dioxide through boiling deeper in the system.

INTRODUCTION

Hydrothermal calcite commonly forms in active geothermal systems, with its formation controlled by f CO_2, pH, temperature, and aqueous calcium ion activity (Garrels and Christ, 1965; Holland and Malinin, 1979; Fournier, 1985); however, for most geothermal systems f_{CO_2} appears to be the limiting factor (Browne and Ellis, 1970; Giggenbach, 1981, 1984, 1988). Since many hydrothermal fluids are close to calcite saturation, indicating that calcite plays a major role as a mineral-gas buffer, the presence or absence of calcite in a hydrothermal mineral assemblage directly reflects the concentration of aqueous carbon dioxide of the coexisting fluid (Ellis, 1969, 1970; Ellis and Mahon, 1977; Arnórsson, 1978; Giggenbach, 1981, 1988). Since boiling and fluid mixing are the main hydrologic processes that affect the concentration of aqueous carbon dioxide in the upper 1 to 2 km of a geothermal system, calcite formation in this environment should be sensitive to the flow of carbon dioxide.

This paper deals with the origins of hydrothermal calcite in active geothermal systems in New Zealand to establish the spatial hydrologic and physico-chemical controls on its formation. Our study focusses calcite formation in the upper 2 km of the Broadlands-Ohaaki geothermal system where calcite is widespread and the hydrologic processes affecting fluid compositions are known. The two examples described herein are calcite replacement of calcium alumino-silicate minerals and calcite deposition in open spaces due to boiling. Fluid inclusion and isotopic ($\delta^{18}O$ and $\delta^{13}C$) data were used to establish the temperature, composition, and origin of calcite-saturated fluids. The results indicate that the occurrence, distribution, and stable isotopes of calcite reflect the concentration and movement of carbon dioxide through a boiling geothermal system.

BROADLANDS-OHAAKI GEOTHERMAL SYSTEM

The Broadlands-Ohaaki geothermal system is one of about twenty known geothermal systems in the Taupo Volcanic Zone (TVZ) of the North Island, New Zealand (fig. 1). The TVZ is a trough-shaped, block-faulted basin formed by extension of Mesozoic graywacke basement, filled with 1 to 3 km of Quaternary volcanics of mostly felsic composition (Cole, 1990). Some of the geothermal systems were explored by drilling, and now Wairakei, Kawerau, and Broadlands-Ohaaki are exploited for energy production. A general overview of the TVZ geothermal systems in

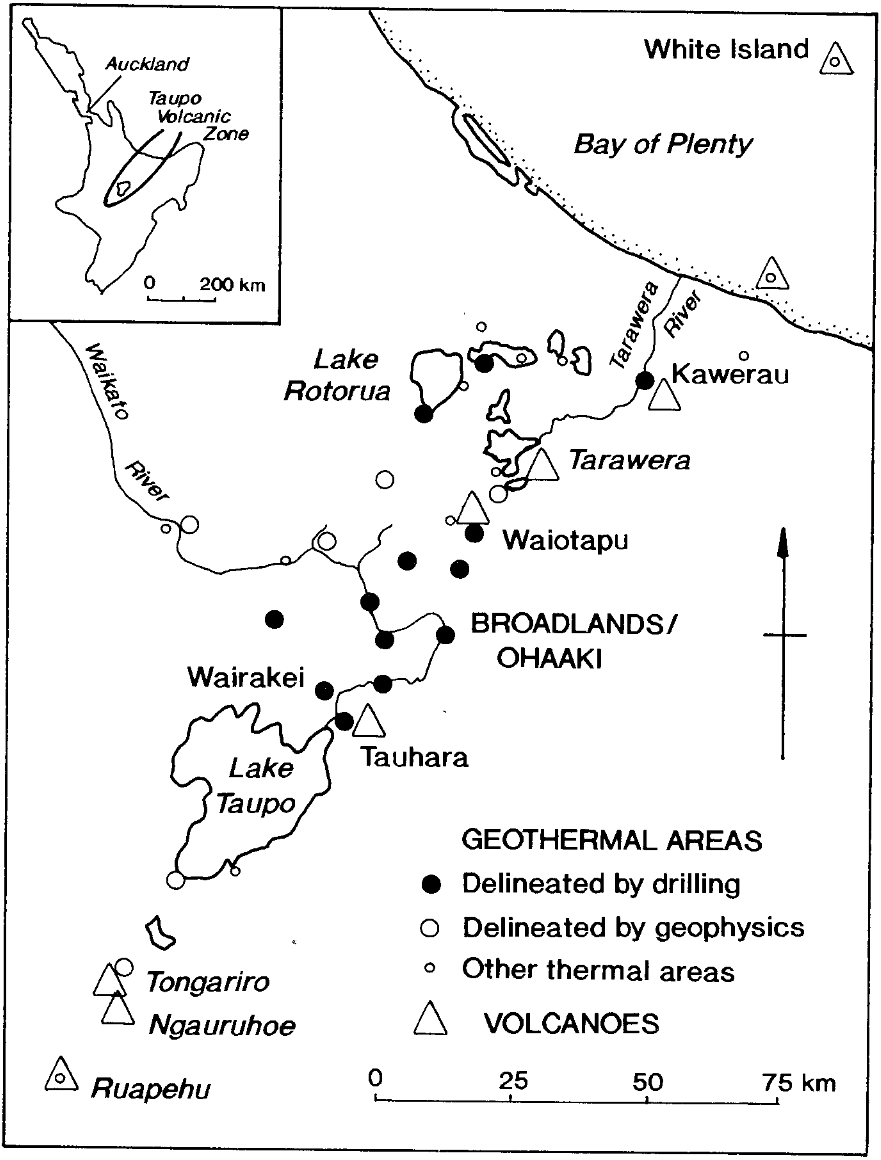

Fig. 1. Location of Broadlands-Ohaaki and other geothermal systems in the Taupo Volcanic Zone, North Island, New Zealand.

terms of geology, geophysics, hydrothermal alteration, and fluid compositions is given by Hedenquist (1986).

Exploration drilling at Broadlands-Ohaaki between 1964 and 1984 resulted in 52 wells (fig. 2), ranging in depth from about 370 to 2600 m. This system has been the subject of numerous studies concerning fluid-rock interaction through the study of hydrothermal minerals (Browne and Ellis, 1970; Browne, 1971a, b, 1973a; Eslinger and Savin, 1973; Blattner, 1975; Wood, 1983; Absar, 1988; Lonker and others, 1990; Simmons and Browne, 1990), fluid compositions and isotopes (Giggen-

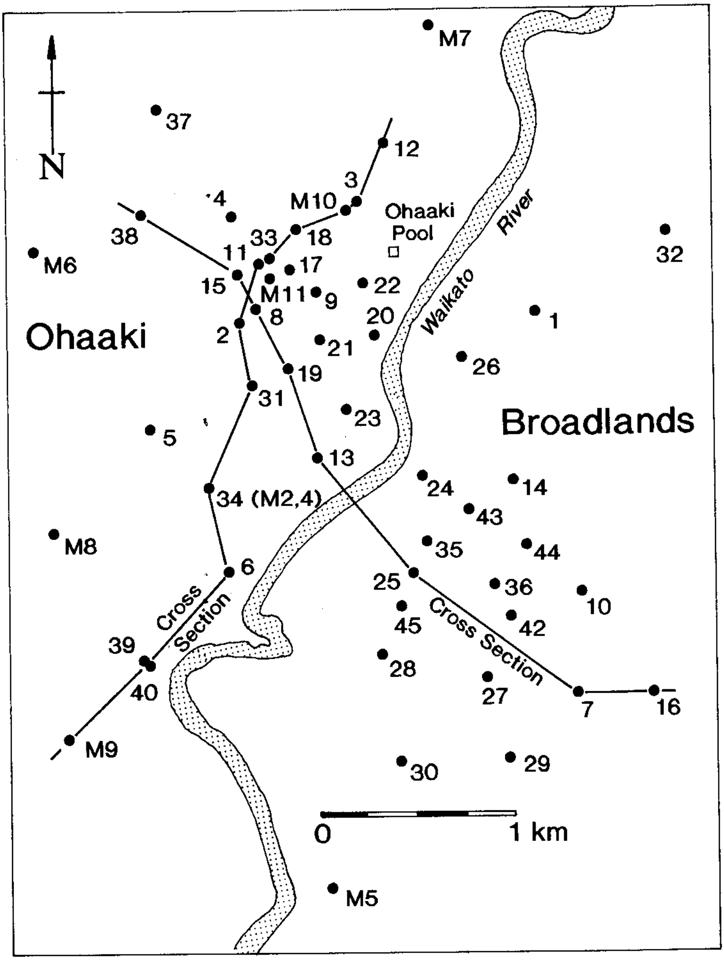

Fig. 2. Plan view map of the Broadlands-Ohaaki geothermal field showing well locations used in construction of cross sections (figs. 3 and 5). The Broadlands and Ohaaki sectors lie beneath the east and west banks, respectively, of the Waikato River.

bach, 1971; Mahon and Finlayson, 1972; Mahon, Klyen, and Rhode, 1980a; Mahon, McDowell, and Finlayson, 1980b; Lyon and Hulston, 1984; Hedenquist and Stewart, 1985; Hedenquist, 1990) and fluid inclusions (Browne, Roedder, and Wodzicki, 1976; Hedenquist and Henley, 1985). The subsurface geology is described by Grindley and Browne (1968). Precious and base metals are depositing at Broadlands-Ohaaki, and the system is likely analogous to those that form epithermal deposits (Browne, 1969, 1971b; Browne and Lovering, 1973; Browne, Rafter, and Robinson, 1975; Ewers and Keays, 1977; Brown, 1986).

A general perspective on the overall understanding of TVZ geothermal systems in terms of fluid composition, mass transfer, processes affecting the distribution of hydrothermal minerals, and the origin of gaseous components is described in a series of papers by Giggenbach (1980, 1981, 1984, 1986, 1988, 1989a, 1989b). Hedenquist (1990) supplies the best current description of Broadlands-Ohaaki and demonstrates how its hydrology affects the fluid composition, which in turn relates to the patterns of hydrothermal alteration; he also describes changes in the system with time. The most significant features are summarized below.

Hydrology.—Cross sections through the Broadlands-Ohaaki system are shown in figure 3 and give a general picture of its hydrology and geochemical structure. Permeability in most of the system is controlled by rock type and fractures. Wells penetrate a layered sequence of rhyolitic to dacitic tuffs, tuff breccias, and lavas, which range in total thickness from 800 to >2000 m. Major faults and related fractures mostly trend northeast, parallel to the major faults of the TVZ.

The shape of the isotherms indicates the position of two fluid upflow centers, the Ohaaki (northwest) and Broadlands (southeast) sectors, separated by the Waikato River. The maximum vertical temperature gradient exists in the center of the upflow zone and is represented by a boiling curve in which water begins to boil at about 310°C and 1800 m depth (Sutton and McNabb, 1977; Hedenquist, 1990). On the margins of the upflows, temperature gradients decrease as thermal fluids mix with cooler steam-heated ground waters. Surface activity is scarce, with the only major feature being Ohaaki Pool, which probably lies along a fault trace (Grindley and Browne, 1968). Most of the deep geothermal fluid appears to flow laterally to the north in the shallow subsurface.

Fluid chemistry.—Table 1 gives representative compositions of the two main fluids, chloride waters and CO_2-rich steam-heated waters, both of which are slightly undersaturated with respect to calcite (Hedenquist, 1990). The deep, parent (that is, unboiled) geothermal fluid at about 2 km depth is a near neutral pH chloride water, containing about 1000 mg/kg Cl and 0.6 m CO_2. Its isotopic composition is $\delta^{18}O_{H_2O} = -4.5$ permil and $\delta D_{H_2O} = -40$ permil, slightly enriched compared to local meteoric water, $\delta^{18}O = -7.0$ permil; $\delta D = -45$ permil (Giggenbach, 1971; Hedenquist and Stewart, 1985). Both carbon dioxide and chloride ions appear to originate from subjacent magmas, hence their input to the

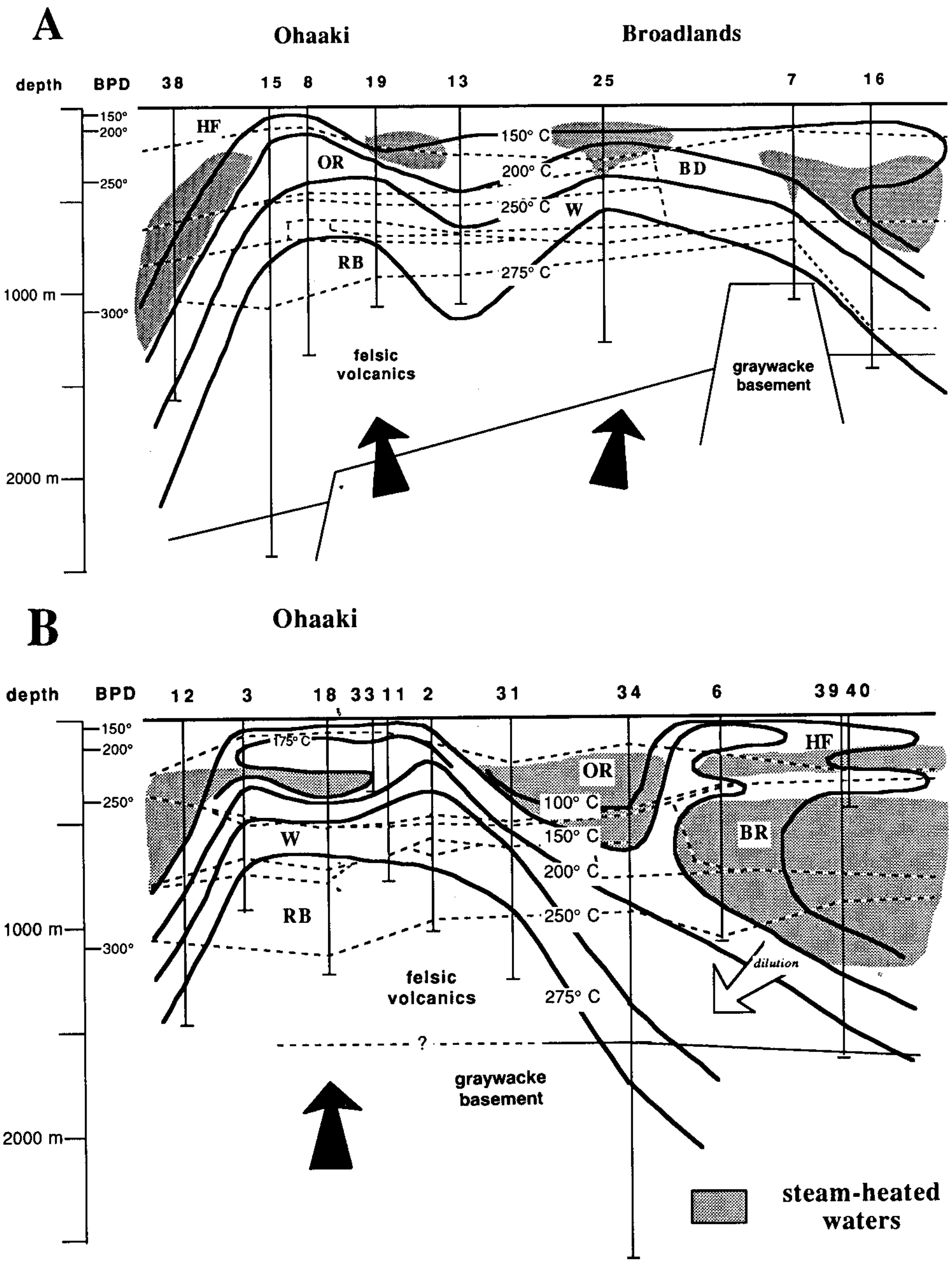
A
Ohaaki
Broadlands
depth
BPD
38
15
8
19
13
25
7
16
150°
200°
250°
300°
1000 m
2000 m
HF
OR
RB
BD
W
150° C
200° C
250° C
275° C
felsic volcanics
graywacke basement
B
Ohaaki
depth
BPD
12
3
18
33
11
2
31
34
6
39
40
150°
200°
250°
300°
1000 m
2000 m
175° C
100° C
150° C
200° C
250° C
275° C
OR
HF
BR
W
RB
felsic volcanics
graywacke basement
?
dilution
steam-heated waters

TABLE 1

Compositions of characteristic hydrothermal waters at Broadlands-Ohaaki: Br-6, CO_2-rich steam-heated water (down hole sample, 850 m, 24-3-86); Br-8, chloride water (well discharge collected from weirbox, 29-2-68; enthalpy = 1201 kJ/kg); Br-12, CO_2-rich chloride water (down hole sample, 635 m, 17-8-87); Br-16, CO_2-rich steam-heated water (down hole sample, 650 m, 8-8-84). Data from Hedenquist (1990)

well	T° C	pH_{lab}	Na	K	Ca	Cl (mg/kg)	SO_4	HCO_3	SiO_2
6	129	7.08	500	40.9	7.3	25	19	17868*	170
8	265	7.9	975	232	3.0	1858	3.5	157	796
12	147	6.4	1359	210	17	1229	23	19389*	234
16	150	6.49	652	56.0	2.4	333	101	9173*	215

* Total carbonate (H_2CO_3 + HCO_3) expressed as bicarbonate.

parent fluid is externally controlled at great depth near the base of the meteoric water convection cell (Giggenbach, 1986, 1989a, b). The concentrations of major cations in the rising fluid are controlled by fluid-rock interaction (Giggenbach, 1984, 1988), the f_{CO_2} being buffered by the generalized reaction:

$$\text{Ca-plagioclase} + CO_2 = \text{calcite} + \text{clay} \qquad (1)$$

(Giggenbach, 1980, 1981). Boiling and mixing supersede fluid-mineral equilibria in controlling the liquid composition at less than about 2 km depth where fluids enter and ascend open fractures. The name "chloride water" refers to the dominant component in the liquid where it discharges at the surface, having lost its dissolved carbon dioxide due to separation of steam and liquid through boiling (carbon dioxide exceeds chloride concentration in the deep parent fluid). These fluids are associated with an assemblage of hydrothermal alteration minerals consisting primarily of quartz, albite, adularia, illite, calcite, chlorite, and pyrite, with rare epidote and wairakite.

Fig. 3. Cross sections of the Broadlands-Ohaaki geothermal system depicting the hydrology as deduced from in situ temperatures and fluid chemistry; redrawn from Hedenquist (1990). Chloride waters ascend through the main upflow zones, whereas CO_2-rich steam-heated waters (stipple pattern) form at shallow depths, descending the sides of the upflow zone. The Rautiwiri Breccia (RB) and the Waiora Formation (W) are permeable and comprise the principal reservoir aquifers, but some formation contacts are also permeable. The Ohaaki Rhyolite (OR), Broadlands Dacite (BD), and other deep ignimbrites are relatively impermeable and form aquicludes. The Huka Falls Formation (HF) caps the sequence and comprises lacustrine sediments and air fall tuffs most of which are impermeable. Northeast trending faults (not shown) crosscut the Ohaaki Sector and form permeable channels along which rising fluids boil. Cross section in northwest-southeast direction is shown in (A), and cross section north-south direction shown in (B). Note that (B) lies parallel to the plane of fault controlled fluid flow. BPD represents the hydrodynamic boiling temperature (see curve B in fig. 9).

The principle diluent of chloride water lies on the margins of the upflow zones (fig. 3) and is a weakly acidic CO_2-rich steam-heated water at about 150°C (Mahon and others, 1980a; Hedenquist and Stewart, 1985; Hedenquist, 1990). This fluid owes its origin to condensation of steam and absorption of carbon dioxide (separated from deeply boiling chloride water) into cool ground waters at shallow depths. The endmember steam-heated composition contains up to 0.3 m CO_2 and no chloride. Intermediate compositions form through mixing of these two endmembers. They may also originate from cooling of the parent chloride fluid (which is carbon dioxide-rich) through mixing with cool ground waters (table 1), without boiling and gas loss. Steam-heated waters are isotopically lighter than chloride waters (fig. 4), with their characteristic alteration assemblage consisting of clays (illite, illite/smectite, smectite, kaolin), calcite, and siderite.

Changes with time.—Fluid inclusions and alteration mineralogy, compared to the present temperatures, indicate that flow patterns within the system have changed over time (Hedenquist, 1990). The greatest changes are apparent in the Broadlands sector where comparison of fluid inclusion and in situ well temperatures indicate this part of the field has cooled considerably (for example, sphalerite-hosted fluid inclusions from Br-16 at 300 m depth have average Th = 240°C, whereas the well temperature

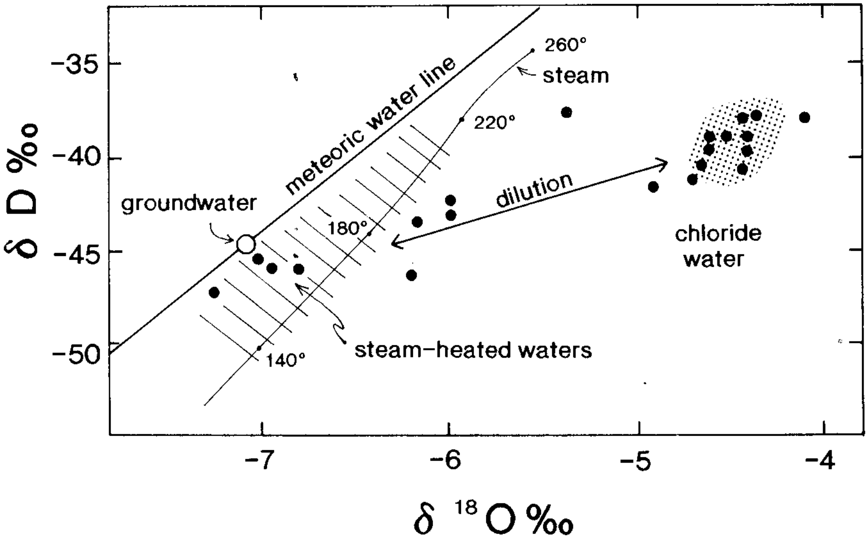

Fig. 4. Oxygen and hydrogen isotope compositions of geothermal fluids (filled circles) at Broadlands-Ohaaki, showing the isotopic differences between chloride water, steam heated water, and local ground water. The isotopic composition of steam fractionated from boiling chloride water, from 260° to 140°C, is also shown. Steam-heated waters have a possible range of isotopic compositions shown by the diagonal line pattern that represents a mixture of steam and local ground water. Redrawn from Hedenquist and Stewart (1985).

at this depth is about 170°C). Most of the alteration minerals in the Ohaaki sector appear to be in equilibrium with the present thermal regime.

SAMPLES AND ANALYTICAL METHODS

Calcite and siderite are the two main hydrothermal carbonates at Broadlands-Ohaaki, and their distribution is shown in cross sections (fig. 5). The only known aragonite occurrence formed at the surface as a precipitate of fluid discharge from well Br-6 (Browne, 1973b). Most samples studied (tables 2, 3, and 4) come from wells shown in figure 5.

Petrologic studies were made on cores, cuttings, and pipe scale from a wide range of temperatures. Two different styles of carbonate occurrence were distinguished (Browne and Ellis, 1970), referred to here as replacement and platy calcite. The adjective replacement refers to hydrothermal carbonate surrounded by rock-forming minerals and volcanic glass (table 2). Relict igneous textures and metastable phases suggest that hydrothermal fluids reacted with a precursor solid phase to produce carbonate. Platy calcite, in contrast, describes the distinct habit of calcite that precipitates in open spaces, infilling natural vugs and fractures or forming pipe scale in geothermal wells. The adjective platy denotes the crystal shape dominated by the basal pinacoid form; other crystal habits of carbonate infilling open space also exist, but these are less common (Browne and Ellis, 1970; Tulloch, 1982) and are not described here.

Fluid inclusions in platy calcite crystals were studied in samples from ten localities at Broadlands-Ohaaki. The homogenization (Th) and melting (Tm) temperatures were measured using a Fluid Inc.-adapted U.S.G.S. gas heating and freezing system (table 3). The thermocouple was calibrated under operating conditions at temperatures of 374.1°, 0.0°, and −56.6°C using Syn Flinc synthetic fluid inclusion standards. The 0.0°C standard was checked daily to confirm the stability of the thermocouple calibration. Freezing runs were always performed first in order to minimize possible changes to inclusions which might be caused by heating (for example, leaking or stretching). For data in table 3, Th is accurate to ±2.0°C, and Tm is accurate to ±0.1°C.

Oxygen and carbon isotope compositions of carbonates were determined commercially through the Institute of Nuclear Sciences, D.S.I.R. (now called The Institute of Geological and Nuclear Sciences, Ltd.), New Zealand, the results of which are given in table 4 together with data from Esslinger and Savin (1973), Blattner (1975), and Absar (1988). Stable isotope data are reported in the δ-notation relative to the SMOW standard for oxygen and PDB standard for carbon. The precision of isotope analyses is better than ±0.2 permil for both oxygen and carbon except where noted in table 4.

REPLACEMENT CALCITE

Replacement calcite occurs with a diversity of other alteration minerals over a temperature range from <125° to >290°C (table 2; fig. 5); its